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PS 0911 5 March 2002 (05.03.2002) AU(71) Applicant (for all designated States except US): **KARALEE RESEARCH PTY LTD [AU/AU]; 7 Karalee Road, Galston, NSW 2159 (AU).**(81) Designated States (national): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.**(84) Designated States (regional): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).**

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.(54) Title: **METHOD FOR TREATING CARBONACEOUS MATERIALS**

(57) **Abstract:** Process for reducing the amount of sulfur-containing impurities in carbonaceous materials are described. One process comprises contacting the materials with an aqueous solution of hydrofluorosilicic acid in the absence of hydrogen fluoride under conditions wherein at least some of the sulfur-containing impurities react with the hydrofluorosilicic acid to form reaction products and separating the reaction products from the carbonaceous materials. Another process comprises contacting the materials with an aqueous solution of hydrofluorosilicic acid in the absence of hydrogen fluoride under conditions wherein at least some of the sulfur-containing impurities react with the hydrofluorosilicic acid to form reaction products, separating the reaction products and the hydrofluorosilicic acid from the carbonaceous materials and subsequently treating the carbonaceous materials with a fluorine acid solution which comprises an aqueous solution of hydrofluorosilicic acid and hydrogen fluoride. A further process comprises treating the carbonaceous materials with a fluorine acid solution which comprises an aqueous solution of hydrofluorosilicic acid and hydrogen fluoride, separating the carbonaceous materials from the aqueous solution of hydrofluorosilicic acid and hydrogen fluoride, and then contacting the carbonaceous materials with an organic solvent capable of dissolving elemental sulfur.

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Method For Treating Carbonaceous Materials

Technical Field

The invention relates to methods for treating carbonaceous materials to remove or substantially decrease the amount of non-carbonaceous impurities therein.

Background of the Invention

5 United States Patent No. 4,780,112 describes a process for treating carbon to reduce the ash therein. The process involves treating the carbon with an aqueous solution of hydrofluorosilicic acid (H_2SiF_6) and hydrofluoric acid (HF), whereby metal oxides in the carbon are converted to metal fluorides and/or metal fluorosilicates, from which carbon is
10 then separated. The process described in United States Patent No. 4,780,112 is effective for removal of metal oxides from carbon, but the present inventor has surprisingly discovered that when carbon that includes sulfur-containing impurities is treated by the process of United States Patent No. 4,780,112, the purified carbon is still contaminated with sulfur. The present inventor has surprisingly discovered that the remaining sulfur is
15 present as elemental sulfur, which in some circumstances is visible when the carbon is viewed under a microscope.

The presence of sulfur in carbon that is intended to be used as a fuel is undesirable, since combustion of the carbon will lead to conversion of the sulfur into sulfur oxides. As a result, the flue gases generated by the combustion of the carbon need to be scrubbed or
20 otherwise substantially freed of the sulfur oxides before they can be discharged into the atmosphere if release of sulfur oxides into the environment is to be avoided.

Accordingly, there is a need for an improved process for treating carbonaceous materials to decrease the amount of non-carbonaceous impurities therein, and in particular there is a need for an improved process for removing or at least substantially reducing the
25 amount of sulfur in carbonaceous materials.

Surprisingly, the present inventor has discovered that the amount of sulfur-containing impurities in carbonaceous materials can be substantially decreased by a process which involves treating the carbonaceous materials with an aqueous solution of hydrofluorosilicic acid, or with an organic solvent capable of dissolving elemental sulfur.

Summary of the Invention

According to a first embodiment of the invention there is provided a process for reducing the amount of sulfur-containing impurities in carbonaceous materials, comprising (a) contacting the materials with an aqueous solution of hydrofluorosilicic acid in the absence of hydrogen fluoride under conditions wherein at least some of the sulfur-containing impurities react with the hydrofluorosilicic acid to form reaction products, and (b) separating the reaction products from the carbonaceous materials.

According to a second embodiment of the invention there is provided a process for reducing the amount of sulfur-containing impurities in carbonaceous materials, comprising

(a) contacting the materials with an aqueous solution of hydrofluorosilicic acid in the absence of hydrogen fluoride under conditions wherein at least some of the sulfur-containing impurities react with the hydrofluorosilicic acid to form reaction products;

(b) separating the reaction products and the hydrofluorosilicic acid from the carbonaceous materials and subsequently

(c) treating the carbonaceous materials with a fluorine acid solution which comprises an aqueous solution of hydrofluorosilicic acid and hydrogen fluoride.

According to a third embodiment of the invention there is provided a process for reducing the amount of sulfur-containing impurities in carbonaceous materials, comprising treating the carbonaceous materials with a fluorine acid solution which comprises an aqueous solution of hydrofluorosilicic acid and hydrogen fluoride, separating the carbonaceous materials from the aqueous solution of hydrofluorosilicic acid and hydrogen fluoride, and then contacting the carbonaceous materials with an organic solvent capable of dissolving elemental sulfur.

As used herein, the term "carbonaceous materials" is to be understood to mean materials which consist predominantly of elemental carbon. Examples of carbonaceous materials include coal including brown coal, coke, lignite, anthracite, charcoal, graphite and the like.

As used herein, unless the context clearly indicates otherwise, the words "comprise", "comprises", "comprising" or other variations thereof shall be understood as

meaning that the stated integer or integers is or are included but that other integers are not necessarily excluded from being present.

Detailed Description of the Invention

In the processes of the first and second embodiments of the invention, the concentration of hydrofluorosilicic acid in the step of contacting the materials with an aqueous solution of hydrofluorosilicic acid under conditions wherein at least some of the sulfur-containing impurities react with the hydrofluorosilicic acid to form reaction products may be in the range of 27% to 37% (w/v or w/w or v/w). The concentration of hydrofluorosilicic acid in the step of contacting the materials with an aqueous solution of hydrofluorosilicic acid under conditions wherein at least some of the sulfur-containing impurities react with the hydrofluorosilicic acid to form reaction products is typically in the range of 28% to 36%, more typically about 32% (w/v or w/w or v/w). The process is usually carried out at atmospheric pressure, but the pressure can also be above or below atmospheric. The temperature may be in the range 28 to 75°C. Typically, the temperature is in the range of 30 to 70 °C, more usually 30 to 40 °C. The reaction time may be in the range 8 to 120 minutes. The reaction time is typically from 10 to 100 minutes, more usually 15 to 30 minutes, still more usually 12 to 16 minutes. The minimum quantity of aqueous hydrofluorosilicic acid employed is typically enough to enable the mixture of it and the carbonaceous materials to be stirred in the acid. Usually, the carbonaceous materials are mixed with at least about twice their weight of the aqueous hydrofluorosilicic acid. More usually, the aqueous hydrofluorosilicic acid is present in an amount of from about 70% to 90% by weight, relative to the total weight of the mixture, still more usually about 70% to 80% by weight of the total weight of the mixture.

In step (a) of the processes of the first and second embodiments of the invention, many metal oxides and some metals present in the carbonaceous materials are converted, at least partially, into the corresponding metal fluorosilicates, with water being the other product. Examples of metals or metal oxides converted to their fluorosilicates are nickel, aluminium, calcium, and mercury and their oxides. Sulfur compounds present are converted, under the reaction conditions, to sulfur dioxide and/or sulfur tetrafluoride.

After step (a) of the processes of the first and second embodiments of the invention, relatively purified carbonaceous materials remain mixed with an aqueous solution containing dissolved metal fluorosilicates. Suitably, this mixture of carbonaceous

materials and metal fluorosilicates may be filtered or centrifuged to separate the relatively purified carbonaceous materials. Optionally, the filtered relatively purified carbonaceous materials may be treated with further aqueous hydrofluorosilicic acid, typically having a concentration of 32% by weight of hydrofluorosilicic acid, to wash out any residual metal fluorosilicates. Separation of the remaining carbonaceous materials from the aqueous phase, and optionally washing the carbonaceous materials, affords a partially purified carbonaceous material which has a lower content of sulfur and metals compared to the original material. The principal impurities typically present in the partially purified carbonaceous materials at this stage are silica and iron sulfide.

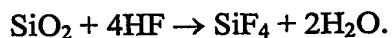
The partially purified carbonaceous material may be further purified to remove other impurities that are not removed in step (a). Thus, the process of the second embodiment provides such a process. In the process of the second embodiment, step (c) is typically a process in accordance with United States Patent No. 4,780,112, the disclosure of which is incorporated herein by reference. Similarly, in the process of the third embodiment, the steps of treating the carbonaceous materials with a fluorine acid solution which comprises an aqueous solution of hydrofluorosilicic acid and hydrogen fluoride, and separating the carbonaceous materials from the aqueous solution of hydrofluorosilicic acid and hydrogen fluoride may be a process as described in United States Patent No. 4,780,112.

In step (c) of the process of the second embodiment, and in the process of the third embodiment, the fluorine acid solution may have a composition lying between the following compositions: 4% w/w H_2SiF_6 , 92% w/w H_2O , 4% w/w HF and 35% w/w H_2SiF_6 , 30% w/w H_2O , 35% HF. In step (c) of the process of the second embodiment, and in the process of the third embodiment, the fluorine acid solution typically has a composition lying between the following compositions: 5% w/w H_2SiF_6 , 90% w/w H_2O , 5% w/w HF and 34% w/w H_2SiF_6 , 32% w/w H_2O , 34% HF. More typically the composition of the fluorine acid solution is about 25% w/w H_2SiF_6 , 50% w/w H_2O , 25% w/w HF. This step is conveniently carried out in two stages as described in US Patent No. 4,780,112. That is, the first stage is conveniently carried out in a stirred reactor at a pressure of approximately 100kPa and a temperature of 40-60°C, and the second stage is conveniently carried out in a tubular reactor at a pressure within the range of about 340 to 480 kPa and a temperature of 65°C to 80°C, more usually about 70°C. Typically, the temperature is maintained at this value by the exotherm of the reaction between silica

present in the carbonaceous materials and hydrogen fluoride. In step (c) the minimum quantity of the fluorine acid solution employed is typically enough to enable the mixture of it and the carbonaceous materials to be stirred. Usually, the carbonaceous materials are mixed with at least about twice their weight of the fluorine acid solution. More usually, the fluorine acid solution is present in an amount of from about 70% to 90% by weight, relative to the total weight of the mixture, still more usually about 70% to 80% by weight of the total mixture.

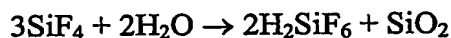
Suitably, in step (c) of the process of the second embodiment, and in the process of the third embodiment, after being mixed with aqueous hydrofluorosilicic acid and hydrogen fluoride, the mixture of the carbonaceous material and the fluorine acid solution may be ultrasonically agitated as described in United States Patent No. 4,780,112, in order for any unreacted ferrous sulfide (which is relatively inert to HF and SiF₄) or other relatively dense impurities to be capable of being separated from the bulk of the relatively purified carbonaceous material, which is less dense than the ferrous sulfide and the aqueous phase. The purified carbonaceous material may be separated from the aqueous phase, optionally washed with aqueous H₂SiF₆, separated, dried to remove excess water (at about 100-110°C) and heated to a temperature within the range of about 250°C to 400°C, or 280°C to 340°C, typically about 310°C, to evaporate any residual hydrofluorosilicic acid remaining on the carbonaceous material, before being used for any desired purpose, such as for a fuel. HF and SiF₄ gases and water vapour are typically evolved during this drying step.

Aqueous fluorine acid separated from carbonaceous materials after it has been contacted with them is relatively enriched in SiF₄ and depleted in HF, compared to the fluorine acid solution before it is contacted with the carbonaceous materials, as a result of the reaction:



This spent aqueous phase, if is recycled to the step of being contacted with the relatively purified carbonaceous material, thus tends to reach a point where it becomes saturated with respect to SiF₄, at which point any further SiF₄ generated as a result of further reaction is evolved as a gas. Conveniently, the reactor in which the fluorine acid solution is contacted with the relatively purified carbonaceous materials includes a means for SiF₄ to be removed from it. Suitably, the spent aqueous phase from this step may be

directed to a holding vessel where any excess SiF_4 is vented from it. The concentration of HF in the spent aqueous phase may be increased by directing a gaseous mixture of HF and SiF_4 into the vessel, whereby the HF is absorbed and the SiF_4 passes through. Vented SiF_4 is conveniently directed to a hydrolyser where it is treated with water to produce
5 H_2SiF_6 , and SiO_2 according to the equation



The silica so produced may be separated from the acid by filtration or any other convenient means. The acid produced in this way is conveniently used in step (a) of the processes of the first and second embodiments.

10 Advantageously, aqueous streams of hydrofluorosilicic acid with or without hydrofluoric acid present, that are generated in processing steps associated with the processes of the present invention, may be directed to an acid still in which the streams are combined and distilled. A gaseous mixture of water, HF and SiF_4 is distilled from the still, these substances being more volatile than the 32% w/w aqueous hydrofluorosilicic
15 acid azeotrope. The gaseous mixture of water, HF and SiF_4 can be directed first to a dehydrating system for removal of water and then the resultant dehydrated gaseous mixture of the HF and SiF_4 may be separated by directing it to a holding vessel which contains a solution of H_2SiF_6 that is saturated with respect to SiF_4 , as described above.

Suitably, the dehydration step for a gaseous mixture of water, HF and SiF_4
20 comprises contacting the gases with a sufficient quantity of anhydrous metal fluoride such as AlF_3 to absorb all the water present. Other metal fluorides that can be used include zinc fluoride and ferrous fluoride. Substantially anhydrous gases may be obtained in this way, together with a hydrated metal fluoride, which may be separated from the anhydrous gases and heated to regenerate substantially anhydrous metal fluoride for recycling to the
25 dehydration step.

In one form of the processes of the first and second embodiments, reaction products separated from carbonaceous materials in step (b) consist of sulfur dioxide and metal fluorosilicates dissolved or suspended in aqueous H_2SiF_6 . Gaseous HCl, derived from inorganic or organic chloride in the carbonaceous material, may also be present. Suitably,
30 these reaction products are directed to a still where they are heated so as to cause gaseous HF, SiF_4 , steam, HCl and sulfur dioxide to be evolved, and so as to cause any metal fluorosilicates present to be concentrated above their solubility limit and to separate as

solids, which can be removed from the still for disposal or re-processing. The gaseous mixture leaving this still may suitably be dehydrated by a process as described above, by contacting it with anhydrous aluminium fluoride, and subsequently passed to an activated carbon filter for removal of sulfur oxides and HCl. The remaining HF and SiF₄ gases, dried and freed of sulfur dioxide, may be directed to the holding vessel for spent aqueous phase from step (c) of a process of the second embodiment, for absorption of the HF.

In the process of the third embodiment the process may further comprise after the separating:

washing the carbonaceous materials to remove any residual acid; and
optionally drying the carbonaceous materials prior to the contacting.

The washing may be with water. The drying may take place at a temperature within the range 100-120°C, typically at 110°C.

In a process of the third embodiment, the organic solvent capable of dissolving elemental sulfur is typically ethanol, benzene, carbon disulfide, either or carbon tetrachloride, or a mixture of two or more of these or other suitable solvent capable of dissolving elemental sulfur. Typically, the solvent is ethanol. The step of contacting the carbonaceous materials with the organic solvent is typically carried out at ambient temperature and atmospheric pressure, but elevated temperatures (e.g. in the range of 30 - 90°C or elevated pressures (e.g. in the range of 1.01 - 5 atm or 1.2-2.5 atm), or both, may also be used. The quantity of solvent used is not critical, but a minimum quantity for practical purposes is a quantity sufficient to enable the mixture to be stirred or agitated.

Suitably, in the process of the third embodiment the organic solvent is contacted with the carbonaceous materials for sufficient time for at least some of the elemental sulfur, which will be present in it after the step of treating the carbonaceous material with the fluorine acid solution, to be dissolved. Conveniently, the solvent is separated from the carbonaceous materials after this time, and is distilled to recover as much as possible for reuse. The treated carbonaceous materials may also be treated to remove any residual solvent, although if the solvent includes no halogen or sulfur atoms, this step can be omitted. Removal of the residual solvent can be by any convenient means such as air blowing or heating (eg at a temperature within the range of 30-100°C the temperature chosen being dependent on the solvent).

The step of separating in the embodiments of the invention may comprise filtering, separating by centrifuging or other suitable separating means.

The processes of the present invention provide several advantages over prior art processes. In addition to providing carbonaceous materials that have significantly lower levels of sulfur than treated carbonaceous materials obtainable by the process of United States Patent No. 4,780,112, processes of the present invention can also result in removal or partial removal of other undesirable substances in carbonaceous materials such as silica, metal oxides and metal sulfides, metals such as mercury and radioactive elements, and inorganic chlorides. For example, if coal contained sulphur at about 8wt% it may be possible to remove this sulphur to a lower level (e.g. about or less than 2wt% or about or less than 1 wt% or about or less than 0.5wt%) by subjecting the coal to one (or more) cycles of the processes of the first to third embodiments. Removal of inorganic chlorides, mercury and radioactive elements, in particular, is more effective with a process of the second embodiment, than with the process of United States Patent No. 4,780,112. Further, processes of the present invention can lower the levels of bound oxygen in the carbonaceous materials and, when applied to coal, can result in an increase in its calorific value, typically by 3-4%.

In the first to third embodiments the carbonaceous materials may be reduced prior to the treating step to granular form which is less than about 4, 3, 2, 1.75, 1.5, 1.25, 1 or 0.75 mm in particle size. At least 80wt%, 85wt%, 90wt%, or 95wt% of the granular particles may be in the range of 5-0.25 mm, 4-0.25 mm, 3-0.25 mm, 2-0.25 mm, or 1-0.25 mm, for example. Alternatively, the carbonaceous material may be treated in its raw form. If the carbonaceous material contains excess moisture it may be dried (e.g. at 60-120°C or 100-120°C) prior to processing so as to remove excess moisture. The drying may be conducted for long enough so as to result in an inherent moisture content of carbonaceous material in the range 3 to 8% w/w, more usually 3 to 5% w/w, for example. Some coals such as lignite which have a high water content usually have to be predried prior to processing. The carbonaceous material may be air dried (e.g. at 60-120°C or 100-120°C) prior to processing by passing hot air over the carbonaceous material, for example. The temperature of the hot air used for drying the carbonaceous material is lower than that which would cause the carbonaceous material to combust.

Brief Description of the Drawings

Figure 1 is a schematic block diagram of a system for purification and combustion of carbonaceous material, incorporating a process in accordance with the present invention.

5 Figure 2 is a schematic block diagram of a still and associated plant for processing an aqueous solution or suspension produced by step (a) of a process of the first or second embodiments of the invention.

Figure 3 is a schematic block diagram of a system for the treatment of carbonaceous materials with a solvent for removal of elemental sulfur, as part of a process of the third
10 embodiment of the invention.

Best Method of Carrying out the Invention

Figure 1 illustrates in schematic block diagram form a system 10 for purification and combustion of carbonaceous materials, incorporating a process in accordance with the present invention.

15 Referring to Figure 1, system 10 includes hopper 20 for holding impure carbonaceous materials which have been reduced to granular form, preferably substantially spherical particles and preferably less than about 2mm in particle size. Associated with hopper 20 is feed unit 25 for conveying carbonaceous materials from hopper 20 to purification reactor 30.

20 Purification reactor 30 is positioned to receive carbonaceous materials from feed unit 25. Purification reactor 30 is also equipped with line 24 to admit an aqueous solution of approximately 32%w/w H_2SiF_6 from a hydrolyser 32. Purification reactor 30 may be a flow through reactor or a stirred or rotating reactor. Typically, purification reactor 30 is a rotating drum reactor. It is also equipped with line 26 for transfer of the contents of
25 reactor 30, after the carbonaceous material has been in contact with the aqueous H_2SiF_6 for a suitable time, to filter 50. Filter 50 is suitably a belt filter and is equipped with line 51 to conduct separated liquids away from filter 50, and conveyor 52 whereby separated solids from filter 50 are transferred to silica removal reactor 55. Reactor 55 is equipped with line 58 for admitting an aqueous fluorine acid solution of HF and H_2SiF_6 from HF
30 absorber 54, and vent line 59 which communicates with hydrolyser 32.

A bottom outlet of reactor 55 communicates via pump 56 and line 57 with a two-stage tubular reactor 65A, 65B, the first stage 65A of which is capable of being agitated ultrasonically. The distal end of reactor 65B discharges into separator 16 which is equipped with takeoffs 66 and 67 adjacent its upper and lower ends respectively. Upper
5 takeoff 66 communicates with centrifuge or belt filter 70 which is capable of separating solid carbonaceous material from aqueous solution. The liquid removal side of centrifuge or belt filter 70 is equipped with line 69 that leads to HF absorber 54, and the solids removal side of centrifuge or belt filter 70 discharges to a system of mixers and separators for washing.

10 The mixer/separator system consists of three mixing tanks 71, 73 and 75 and three separators, such as centrifuges or belt filters, 72, 74 and 76 arranged so that carbonaceous materials can flow sequentially from mixing tank 71 to separator 72, then to mixing tank 73 followed by separator 74, then to mixing tank 75 and separator 76. The system is arranged so that aqueous phase moves essentially counterflow to the solids.

15 The solids exit of final separator 76 is connected to a drying system which consists of mixing vessel 77, tubular reactor 78 and solids separator 79. The liquid exit of the mixer/separator system is from separator 72 and communicates with a still 80. Separator 79 has a vapour off-take that also communicates with still 80, which is equipped with a jacket heater, vapour outlet 81 and a bottom outlet leading to solids separator 98.

20 Optionally, a solvent extraction system such as described below with reference to Figure 3 may be installed between the solids exit of separator 76 and mixing vessel 77, as shown in phantom in Figure 1.

Vapour outlet 81 of still 80 is connected via pressure fan 82 and mixer 83 to gas dehydration reactor 84. Mixer 83 is also equipped with a connection (not shown)
25 whereby hot gases can be admitted to it. Downstream of dehydration reactor 84 is separator 86 with anhydrous gas takeoff 87 which is connected to HF absorber 54. Separator 86 is also connected to solids transfer line 88 which communicates with fluoride drier 89. Fluoride drier 89 is equipped with water removal lines 91a, 91b and fluoride supply line 90 for transferring substantially anhydrous metal fluoride(s) from
30 drier 89 to mixer 83.

When system 10 is in use, carbonaceous material from hopper 20 is transferred via feed unit 25 to reactor 30. Suitably, the transfer of carbonaceous material via feed unit 25

is by a system of a plurality of disks within a tube or pipe, the disks being approximately the internal diameter of the tube or pipe and connected by a cable whereby they can be drawn through the tube or pipe. A suitable system is marketed under the name "Floveyer" by GPM Australia Pty Ltd of Leichardt, New South Wales. The transfer of material may be continuous or batchwise. Also supplied to reactor 30 is aqueous H_2SiF_6 , from hydrolyser 32 via line 24. Reactor 30 is typically at a temperature of about 30°C and atmospheric pressure.

Carbonaceous material is contacted with the aqueous H_2SiF_6 in reactor 30 for a time sufficient for at least some of any sulfur-containing impurities in the carbonaceous material to react and dissolve. This may be achieved in a flow-through reactor by controlling the flow rate of the reactant aqueous solution to provide a sufficient residence time in reactor 30. Alternatively, the process may be carried out batchwise, with sufficient time being allowed for reaction of each batch. Typically a suitable reaction time is in the range of 10 to 100 minutes, more typically 15 to 30 minutes, still more typically 12 to 16 minutes.

The mixture of aqueous acid and carbonaceous materials from reactor 30 is transferred via line 26 to filter 50 in which the aqueous phase containing aqueous hydrofluorosilicic acid and dissolved metal fluorosilicates, and the like, is separated from partially purified carbonaceous materials. The aqueous phase is transferred by a line 51 to still 110 (not shown in Figure 1) for separation of metal fluorides as described in more detail below with reference to Figure 2.

Partially purified carbonaceous material is transferred via conveyer 52 to reactor 55 where it is mixed with an aqueous fluorine acid solution comprising aqueous hydrofluorosilicic acid and hydrogen fluoride so that partially purified carbonaceous materials from purification reactor 30 can remain in contact with the aqueous fluorine acid solution for a sufficient time for at least some of any silica in the partially purified carbonaceous material to be dissolved. Reactor 55 is typically maintained at a pressure in the range of about 100-135 kPa and a temperature of about 70°C . Residence time of the carbonaceous material in reactor 55 is typically from 10 to 20 minutes, more typically about 15 minutes.

From reactor 55 the mixture of the carbonaceous material and aqueous fluorine acid solution is passed via pump 56 to first stage tubular reactor 65A and thence to second

stage 65B. The temperature in tubular reactor 65A, 65B is typically about 70°C and the pressure is typically from 350 to 500 kPa. In first stage reactor 65A the suspension of carbonaceous material in aqueous acid is agitated sufficiently for any FeS and other relatively dense material present to be separable at separator 16 at the end of second stage
5 reactor 65B. In second stage tubular reactor 65B, the mixture is not ultrasonically agitated. From a lower portion of separator 16 a slurry of solids which are rich in FeS is removed via line 67. A slurry of carbonaceous material in aqueous hydrofluorosilicic acid is removed from an upper portion of separator 16 via line 66 and transferred to centrifuge or belt filter 70 where aqueous acid is removed, leaving a carbonaceous
10 material stream to be transferred to the washer/separator system.

In this system, carbonaceous material is washed with aqueous hydrofluorosilicic acid which flows through the system in the opposite direction to the direction of flow of the carbonaceous materials. That is, the fresh supply of aqueous hydrofluorosilicic acid is supplied from hydrolyser 32 to mixing tank 75 where it mixes with carbonaceous material
15 and is separated in separator 76. From separator 76 the aqueous phase is transferred to mixing tank 73 where it is mixed with carbonaceous material entering that mixing tank, and separated therefrom in separator 74. The aqueous phase separated in separator 74 is transferred to mixing tank 71 where it is mixed with carbonaceous material leaving centrifuge or belt filter 70. The solids and liquids in mixing tank 71 are separated in
20 separator 72, the solids being transferred to mixing tank 73 and the liquids being transferred to still 80. Solids leaving separator 76 are thus washed solids, and liquid leaving separator 72 is relatively impure.

Carbonaceous material leaving the final separator 76 in the sequence of vessels is admitted (optionally via a solvent extraction system) to a drying system which consists of
25 mixing vessel 77 and steel tube reactor 78. The carbonaceous material entering mixing vessel 77 is mixed with oxygen-depleted combustion gases and transferred to reactor 78 where it is baked under inert atmosphere, typically at about 310°C, to remove the remaining hydrofluorosilicic acid from the surface of the carbonaceous material. The hydrofluorosilicic acid is removed as gaseous hydrogen fluoride and silicon tetrafluoride,
30 together with steam, which gases are directed to still 80 after the gases and the dried solids are separated in separator 79. Dried solids exiting separator 79 are purified carbonaceous materials which are suitable for use as a combustible fuel. System 10 further includes carbonaceous materials storage container 93 from which dried

carbonaceous material can be supplied to furnace and gas turbine system 95. Optionally, system 10 includes a solvent extraction stage as described below with reference to Figure 3, between separator 79 and storage container 93 as illustrated in phantom in Figure 1.

Aqueous phase removed from centrifuge or belt filter 70 is passed to HF absorber 54 where gases from drier 84 and separator 86 are admitted for absorption of HF to generate the fluorine acid solution to be supplied to silica removal reactor 55. Also supplied to HF absorber 54, via line 53, and HF and SiF₄ gases from system 100 as illustrated in Figure 2 and described in more detail below. Gases leaving HF absorber 54 pass to hydrolyser 32 to which water 36 is added in sufficient amount to produce aqueous H₂SiF₆ of the desired concentration for use in reactor 30. Silica generated in hydrolyser 32 is removed via a bottom outlet.

Aqueous acid leaving the washer/separator system at separator 72 is transferred to still 80 where it is heated to sufficient temperature (typically 105 to 110 °C) to cause hydrogen fluoride and silicon tetrafluoride gases to be liberated from the aqueous solution and any metal fluorides that had been contained in the aqueous phase to separate out as solids. It will be appreciated that the pressure difference across fan 82 will affect the pressure in still 80 and hence its temperature. The separated solids are removed from still 80 via separator 98. Still 80 is typically heated by exhaust gas from gas turbine 85. Vapours from mixing vessel 77 and separator 79 are typically returned to still 80 and provide a further source of heat.

Gases leaving still 80 are passed via line 81 and pressure fan 82 to mixer 83 in which they are mixed with substantially anhydrous AlF₃. The mixture is passed through tubular dehydration reactor 84 leading to removal of substantially all the water from the gaseous phase, thereby producing a substantially anhydrous gaseous mixture of HF and SiF₄ which is transferred from dehydration reactor 84 to HF absorber 54 via line 87. Moist AlF₃ produced in dehydration reactor 84 is transferred to AlF₃ drier 89 in which the moist AlF₃ is heated. Water vapour generated by this heating is removed at 91a and 91b, and substantially anhydrous AlF₃ is recycled via line 90 to mixer 83. Exhaust gases from gas turbine 95 are conveniently used for the purpose of heating drier 89.

Figure 2 illustrates in schematic block diagram form a system 100 comprising a still and associated plant for processing an aqueous solution or suspension produced by step (a) of a process of the first or second embodiments of the invention.

Referring to Figure 2, system 100 includes still 110 equipped with supply line 115 communicating with filter 50 as illustrated in Figure 1. Still 110 is also equipped with jacket heater 112, vapour outlet 120 and a bottom outlet connected to level controlled separator 150. Gas outlet 120 communicates via pressure fan 125 to water removal
5 system 130, the gas outlet of which is connected to a pair of activated carbon filters 135, 136 which are connected to steam condenser 140. Condenser 140 is equipped with vent 145 and drain 146. Carbon filters 135, 136 are respectively equipped with gas outlets 138 and 139, and are connected to steam supply line 133.

In use, aqueous phase leaving reactor 30 as illustrated in Figure 1 and separated
10 from solids at filter 50 is admitted to still 110 via line 115, and still 110 is heated by jacket heater 112 to a temperature sufficient for gases comprising HF, SiF₄, sulfur dioxide and water vapour to be evolved from still 110 and leave via outlet 120. These gases are pressurised by fan 125, typically to a pressure in the range of about 70-140 kPa, and passed into a water removal system 130 including anhydrous aluminium fluoride, as
15 described above with reference to Figure 1. The temperature of still 110 is dependent on the pressure generated by fan 125, but is typically in the range of 105 to 110 °C. In water removal system 130, water vapour is substantially removed and substantially anhydrous gases leave the water removal system and are admitted to one or the other of activated carbon filters 135, 136. As the gases pass through the activated carbon filter, sulfur
20 dioxide and certain other gases that may be present, such as HCl, are absorbed by the activated carbon, generating a stream of gaseous HF and SiF₄ which is removed at gas outlet 138 or 139 and transferred to HF absorber 54 of system 10 as shown in Figure 1, via line 53 thereof. Conveniently, activated carbon filters 135, 136 are used in tandem so that one of the activated carbon filters is on-stream and being contacted with gases
25 leaving water removal system 130 while the other activated carbon filter is off-stream and is being heated to desorb sulfur dioxide and other absorbed species such as hydrogen chloride. The heating is by means of steam admitted via line 133. The desorbed species are transferred from the activated carbon filter which is being cleaned in this way to steam condenser 140 where the steam is condensed and removed, together with dissolved SO₂
30 and any HCl present, via drain 146.

Liquids in still 110 become more concentrated as a result of the heating and evaporation of gases therefrom, until a point where dissolved inorganics in the liquids exceed their solubility limit. Inorganic solids accumulating in still 110 can be removed

from the bottom outlet of the still and passed to a level controlled separator 150 from which solids can be separated from the liquid phase by any convenient means and can be directed either to disposal or to a reprocessing plant to obtain useful materials therefrom. The separated liquids can be returned to still 110.

5 Figure 3 illustrates in schematic form a system 200 for treatment of partially purified carbonaceous materials with a solvent capable of dissolving elemental sulfur, in accordance with a process of the third embodiment of the invention.

Referring to Figure 3, system 200 includes treatment vessel 210 which is equipped with carbonaceous material inlet 215 and solvent inlet 216, as well as outlet 218 to permit
10 transfer of carbonaceous material and solvent from treatment vessel 210 to solid/liquid separator 220. Separator 220 may be any convenient form of separator such as filter or centrifuge, or settler. Separator 220 is equipped with a solids removal outlet connected to stripper 230 and a liquids outlet 225 connected to a still (not shown). Stripper 230 is equipped with a heater (not shown), vapour off-take line 237 and solids outlet 235.

15 When system 200 is in use, carbonaceous material which has been treated with a fluorine acid solution as described, for example, in United States Patent No. 4,780,112, and solvent are charged into treatment vessel 210 where they are mixed and allowed to remain in contact for sufficient time for at least part of any elemental sulfur present in the carbonaceous materials to be dissolved by the solvent. The solvent is typically ethanol,
20 but may be any other solvent which is capable of dissolving elemental sulfur, or a mixture of such solvents. The treatment in the treatment vessel 210 is typically at ambient temperature and atmospheric pressure. After an appropriate contact time, the contents of treatment vessel 210 are conveyed via bottom outlet 218 to separator 220 in which the solids phase is separated from the solvent phase. The solids phase is transferred to
25 stripper 230 where it is heated, causing residual solvent to evaporate. Suitably, the temperature of heating is at or about the boiling point of the solvent used. After sufficient heating time to cause substantially all of the residual solvent to evaporate from the carbonaceous material in stripper 230, the dried carbonaceous material is discharged via outlet 235 for further processing or for use.

30 Liquids leaving separator 220 and vapour leaving stripper 230 may be passed to a solvent still (not shown) in which the solvent is distilled for recovery and reuse, the other major product in the still being elemental sulfur which is removed for disposal or sale.

Example

Coal samples processed by a process as described in United States Patent No. 4,780,112 were dried and examined under an electron microscope. They were observed to contain sulfur in two forms, pyrite and elemental sulfur.

- 5 A raw high-sulfur coal sample was treated with about twice its weight of 32% w/w aqueous hydrofluorosilicic acid for 30 minutes at ambient temperature, then dried and treated with an aqueous fluorine acid solution as described in United States Patent No. 4,780,112. After separation of the solids they were again dried and examined under the electron microscope. No elemental sulfur was visible.

Claims

1. A process for reducing the amount of sulfur-containing impurities in carbonaceous materials, comprising

5 (a) contacting said materials with an aqueous solution of hydrofluorosilicic acid in the absence of hydrogen fluoride under conditions wherein at least some of said sulfur-containing impurities react with said hydrofluorosilicic acid to form reaction products, and

(b) separating said reaction products from said carbonaceous materials.

10 2. A process for reducing the amount of sulfur-containing impurities in carbonaceous materials, comprising

(a) contacting said materials with an aqueous solution of hydrofluorosilicic acid in the absence of hydrogen fluoride under conditions wherein at least some of said sulfur-containing impurities react with said hydrofluorosilicic acid to form reaction products;

15 (b) separating said reaction products and said hydrofluorosilicic acid from said carbonaceous materials and subsequently

(c) treating said carbonaceous materials with a fluorine acid solution which comprises an aqueous solution of hydrofluorosilicic acid and hydrogen fluoride.

3. A process for reducing the amount of sulfur-containing impurities in carbonaceous materials, comprising:

20 treating said carbonaceous materials with a fluorine acid solution which comprises an aqueous solution of hydrofluorosilicic acid and hydrogen fluoride,

separating said carbonaceous materials from said aqueous solution of hydrofluorosilicic acid and hydrogen fluoride, and then

25 contacting said carbonaceous materials with an organic solvent capable of dissolving elemental sulfur.

4. The process of claim 1 or 2 wherein the concentration of hydrofluorosilicic acid in the step (a) is in the range of 27% to 37% (w/v or w/w or v/w).

5. The process of claim 1 or 2 wherein the concentration of hydrofluorosilicic acid in the step (a) is in the range of 28% to 36% (w/v or w/w or v/w).

6. The process of claim 1 or 2 wherein the temperature of step (a) is in the range of 28 to 75°C.
7. The process of claim 1 or 2 wherein the temperature of step (a) is in the range of 30 to 70 °C.
- 5 8. The process of claim 1 or 2 wherein the reaction time of step (a) is in the range of 8 to 120 minutes.
9. The process of claim 1 or 2 wherein the reaction time of step (a) is in the range of 10 to 100 minutes.
- 10 10. The process of claim 1 or 2 wherein in step (a) the carbonaceous materials are mixed with at least about twice their weight of the aqueous hydrofluorosilicic acid.
11. The process of claim 1 or 2 wherein after step (b) treating said separated carbonaceous materials with further aqueous hydrofluorosilicic acid to remove residual metal fluorosilicates.
12. The process of claim 2 or 3 wherein the fluorine acid solution has a composition
15 lying between the following compositions: 4% w/w H_2SiF_6 , 92% w/w H_2O , 4% w/w HF and 35% w/w H_2SiF_6 , 30% w/w H_2O , 35% HF.
13. The process of claim 2 or 3 wherein the fluorine acid solution has a composition lying between the following compositions: 5% w/w H_2SiF_6 , 90% w/w H_2O , 5% w/w HF and 34% w/w H_2SiF_6 , 32% w/w H_2O , 34% HF.
- 20 14. The process of claim 2 or 3 wherein the fluorine acid solution has a composition of about 25% w/w H_2SiF_6 , 50% w/w H_2O , 25% w/w HF.
15. The process of claim 2 wherein in step (c) the carbonaceous materials are treated with at least about twice their weight of the fluorine acid solution.
16. The process of claim 3 wherein in step (a) the carbonaceous materials are treated
25 with at least about twice their weight of the fluorine acid solution.
17. The process of claim 1 wherein after step (b) comprising washing said separated carbonaceous material with aqueous H_2SiF_6 , and heating said washed carbonaceous material at a temperature in the range of about 250°C to about 400°C to evaporate any residual hydrofluorosilicic acid remaining on the carbonaceous material.

18. The process of claim 3 wherein the organic solvent capable of dissolving elemental sulfur is ethanol, benzene, carbon disulfide, either or carbon tetrachloride, or a mixture of two or more of these.
19. The process of claim 3 wherein the step of contacting the carbonaceous materials
5 with the organic solvent is at ambient temperature and atmospheric pressure.

FIGURE 1

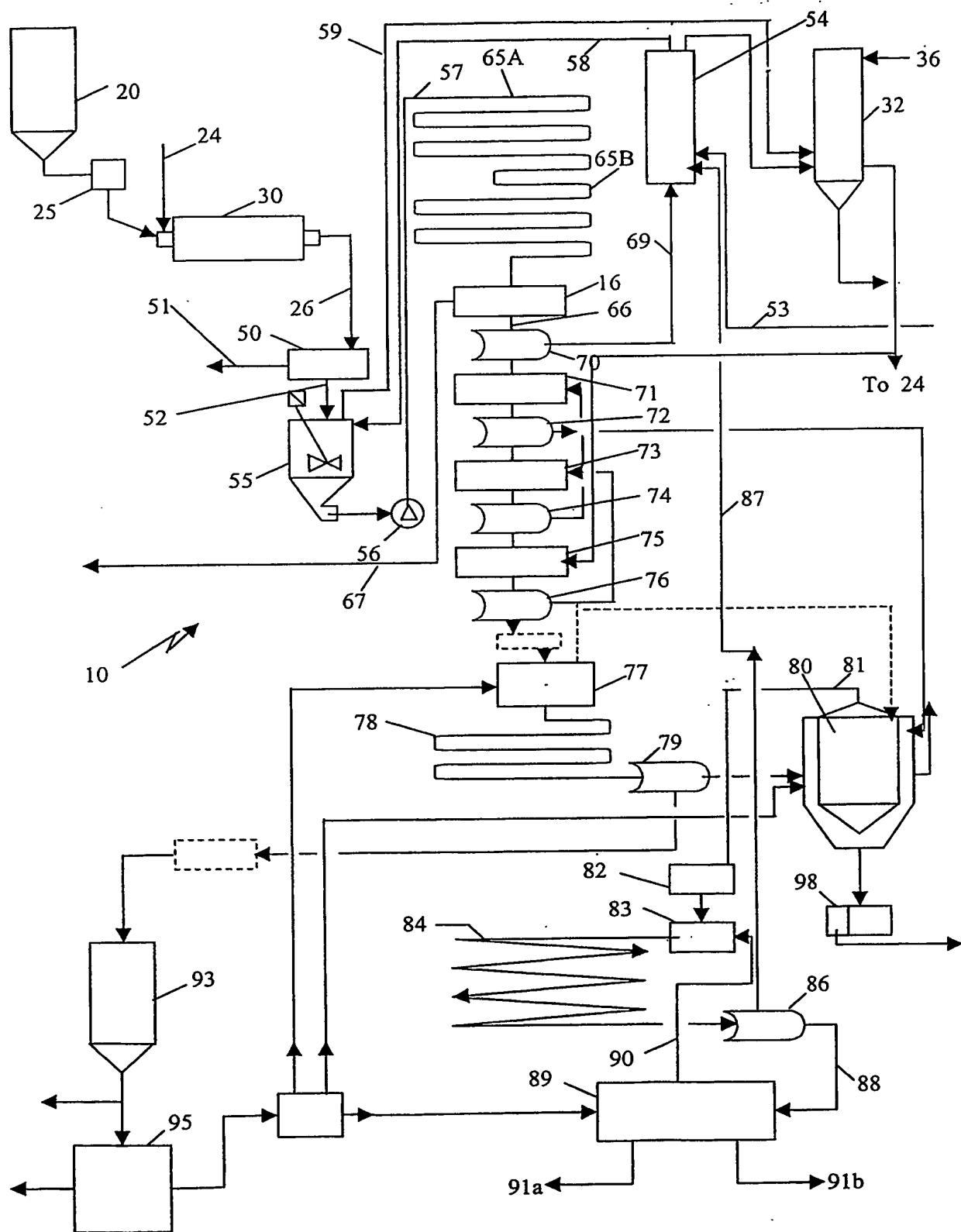


FIGURE 2

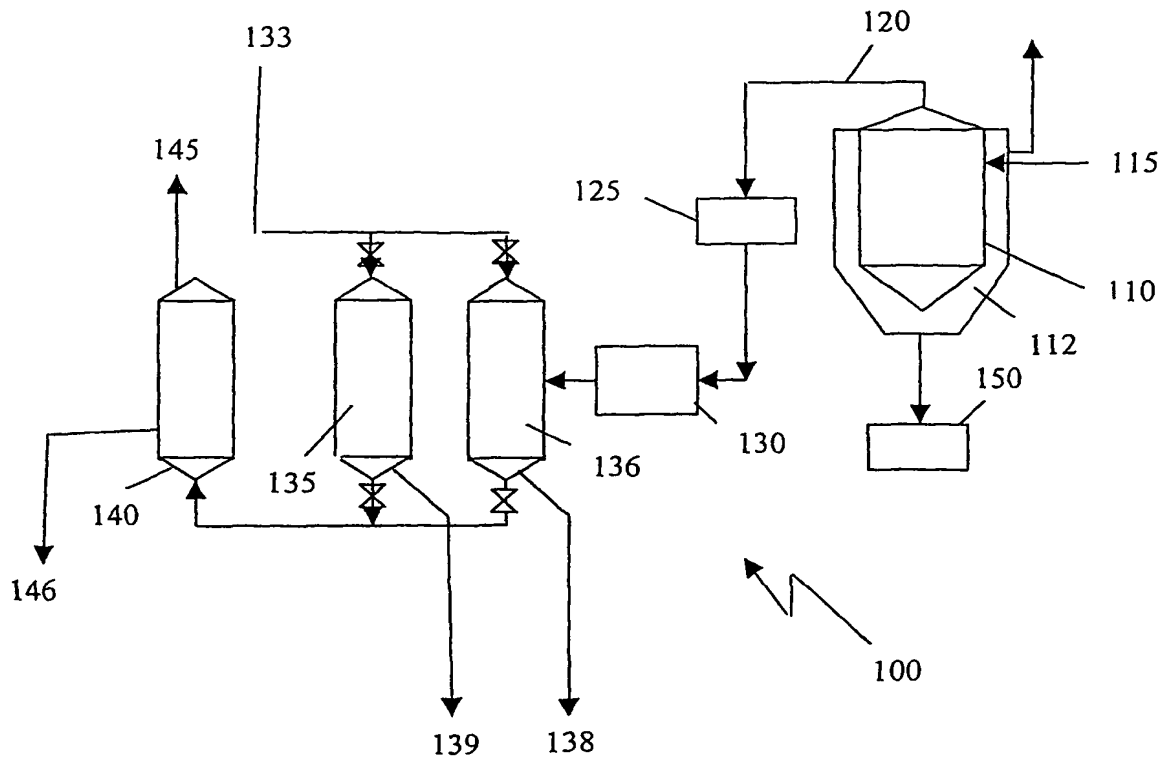
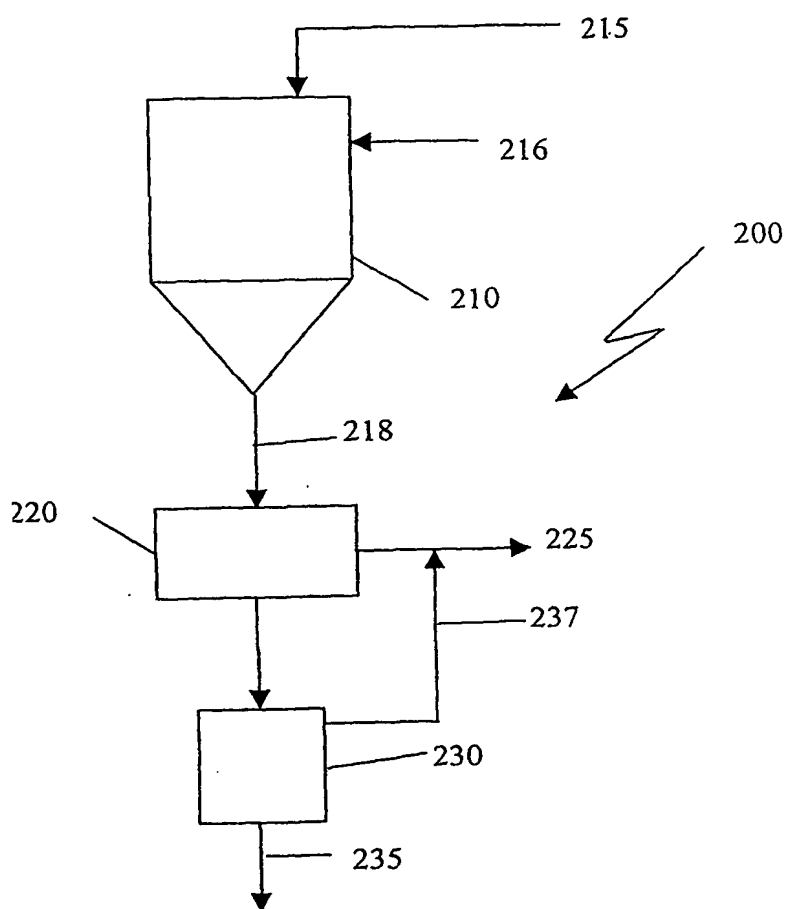


FIGURE 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU03/00258

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : C10L 9/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
DWPI: C10L 9/IC Keywords: hydrofluorosilicic acid, hydrofluorosili+, +sulphur+, +sulfur+, +fluor+		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 1537286 A (BARNEBEY) 12 May 1925 See column 1, lines 31-45	1
A	US 4780112 A (LLOYD ET AL) 25 October 1988 See whole document	1-19
A	EP 0016624 B (KINNERET ENTERPRISES LIMITED) 25 May 1983 See whole document	1-19
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 18 March 2003		Date of mailing of the international search report 08 APR 2003
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer THARU FERNANDO Telephone No : (02) 6283 2486

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU03/00258

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0120499 A (JAPAN AUSTRALIA PROCESS COAL COMPANY) 3 October 1984 See whole document	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU03/00258

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
US	1537286	NONE			
US	4780112	AU	55848/86	BR	8605483
		CN	86101114	EP	215029
		WO	8604917	ZA	8601243
EP	0016624	AR	221757	AU	5623680
		JP	55133487	ZA	8001403
EP	0120499	AU	2620084		
					END OF ANNEX